

INITIATION OF LOCALIZED CORROSION AT THE NANOMETER SCALE

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The objectives of this paper are the following:

- to summarize the recent progress in the understanding of the growth mechanisms and the structure of passive films on metals and alloys,
- to present recent data on the early stages of passivity breakdown and localized corrosion obtained by Scanning Tunneling Microscopy (STM),
- to discuss the contribution of STM data to the understanding of passivity, passivity breakdown and localized corrosion.

The data which will be presented have been obtained by STM and EC-STM (*in situ* Electrochemical Scanning Tunneling Microscopy), combined with XPS (X-ray Photoelectron Spectroscopy) for chemical analysis of the passive films. The metals and alloys which have been studied include Cu, Ni, Cr, ferritic and austenitic stainless steels. For the initiation of pitting the emphasis will be placed on Ni.

I. Recent progress in the understanding of the growth mechanisms and the structure of passive films.

The general conclusions which can be drawn from the studies of passive films by high resolution STM are as follows:

- passive films are crystalline (on Cu, Ni, Cr, FeCr and FeCrNi alloys),
- crystallization is strongly dependent on potential and time (ageing of passive layers favors their crystallinity),
- epitaxial growth is generally observed,
- surface defects, such as steps, are preferential oxide nucleation sites,
- the preferred crystallographic direction of oxide growth is governed by the lowering of the surface energy, a process in which the hydroxylation of the oxide surface by dissociative adsorption of water plays a major role.

II. Early stages of passivity breakdown and localized corrosion

STM is a new tool to investigate the initiation of localized corrosion at the nanometer scale. The following aspects will be addressed:

- the effect of Cl⁻ on the structure of passive films. Experiments have been performed in which Ni single crystal surfaces were fully passivated in Cl⁻-free

solution prior to the addition of Cl⁻, or in which passivation was done in Cl⁻-containing solutions. In both cases, it appears that the atomic structure of the passive layer is identical to the one obtained in the absence of Cl⁻.

- the detection of nanoscopic pits in the early stages of localized corrosion. After passivation of Ni at 0.85 V/SHE in Na₂SO₄ at pH = 3 for 30 min., and subsequent addition of 50mM Cl⁻, nanoscopic metastable pits were detected, with a lateral size ~ 20nm and a depth of ~ 2nm (~ 10⁻¹⁴ C per pit).

- the measurement of the density of metastable pits. A high density of pit nuclei was observed in the early stages of pitting (of the order of 10⁹/cm²).

- the identification of the location of pit nucleation. The STM measurements on well defined surfaces of passivated nickel revealed that pit nuclei are formed preferentially at step edges of the metal surface.

- the investigation of the mechanisms of depassivation/repassivation of metastable pits. The structure of the passive film in metastable pits was measured by STM and was found to be identical to the one measured on the non-pitted surface.

The contribution of STM data to the understanding of passivity, passivity breakdown and the initiation of pitting will be discussed in the light of the above results.